Nanofibrillated cellulose (CNF) freestanding films

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Abstract

Environmental pollution and global warming have been the main problems in human development. Therefore, the exploration of sustainable and green energy sources has been one of the most challenging issues today. Semi-transparent organic solar cell (OSC) has great potential in energy source and for applications of "electronics everywhere". Nanofibrillated cellulose (CNF) is a sustainable material with many beneficial properties which makes it a suitable candidate as carrier material in multi-layered systems. The main objective of this project is to produce the best freestanding CNF films which, after being functionalized with silver nanowires (AgNW), could be used in the development of sustainable electronic devices like organic solar cells. To produce the best freestanding CNF films, three different methods were used: gel, drop casting and spraying. Furthermore, CNF gel and solution with different surface charges were tested, and the substrate on which the CNF was applied was also changed. The electronic properties and structure of the most promising samples were investigated using solvent tests, microscopy, ellipsometer and four-point sheet resistance measurements. The best film produced was made using the spray-method on a glass surface. This film showed excellent properties of tensile strength, flexibility, and transparency (79.43 % light transmission at 550nm). The sheet resistance decreased with increasing concentration of AgNWs in the ink. The film which had the smallest sheet resistance, thus more conductive, had an average sheet resistance of 13.24 $\Omega/square$. However, the light transmission of the film decreased to 50 % when AgNW ink was applied.

Keywords: Cellulose, film, organic solar cell, sustainable, spraying

Contents

1. Introduction

Environmental pollution and global warming have been the main problems in human development due to excessive exploitation and consumption of fossil fuels. Thus, the exploration of sustainable and green energy sources has been one of the most challenging issues today. Because of its properties, solar energy has been considered as one of the most promising candidates to meet the energy needs of human society.[1] Also, the application of green, renewable and sustainable materials has become increasingly important for producing various high-value products with low environmental impact.

Semi-transparent organic solar cell (OSC) has attracted more and more attention due to its great potential in energy source in door, electricity-generating windows, building-integrated photovoltaics and agricultural greenhouse. An ideal semi-transparent solar cell should have a high utilization efficiency of ultraviolet and near infrared photons, and maintain an appropriate balance between absorption and transparency in visible light range.[1] In this context, cellulose is a sustainable material with many beneficial properties, such as lightweight, transparency, and flexibility, which makes it a suitable candidate as carrier material in multi-layered systems. Being a perfect candidate for advanced applications in thin-film organic solar cells, supercapacitors, or sensors.[2]

Therefore, the main objective of this project is to produce the best freestanding CNF films (transparent, thin, resistant, and flexible) which, after being functionalized with silver nanowires (AgNW), could be used in the development of sustainable electronic devices like organic solar cells. Different methods and materials will be used to produce the films, and the electronic properties and structure of the most promising samples will be investigated using solvent tests, microscopy, ellipsometer and four-point measurements.

2. Materials and Methods

2.1. Nanofibrillated cellulose (CNF)

Cellulose is the most abundant polymeric raw material on earth. Cellulose is basically constituted by repeating β (1,4)-bound D-glucopyranosyl units (anhydroglucose unit, AGU) in the 4C1-chain configuration, in which every monomer unit is corkscrewed at 180° compared to its neighbours .[3] As a material, cellulose is inherently renewable and biodegradable, making it a material with great potential, especially in times where our environmental footprint should be even more considered than ever before.[2]

Nanocellulose can be defined as cellulose whose at least one dimension (length, diameter, or height) is at nanoscale regardless of their source or manufacturing methods. Among all the major categories of nanocellulose, nanofibrillated cellulose (CNF) have always been attractive to the researchers due to its superior properties including large specific surface area, high stiffness, high strength, low weight, high biocompatibility, and easy film-forming capability. Thus, the applications of CNFs include sensors, food packaging, electrode, micro batteries and organic solar cells.[4] The CNF-gel used in this report were produced from chemically bleached wood fibers (60 % Norwegian spruce and 40 % Scots pine, Domsjo AB, Sweden), the wood-pulp fibres were chemically treated with a TEMPO-mediated oxidation reaction.[2]

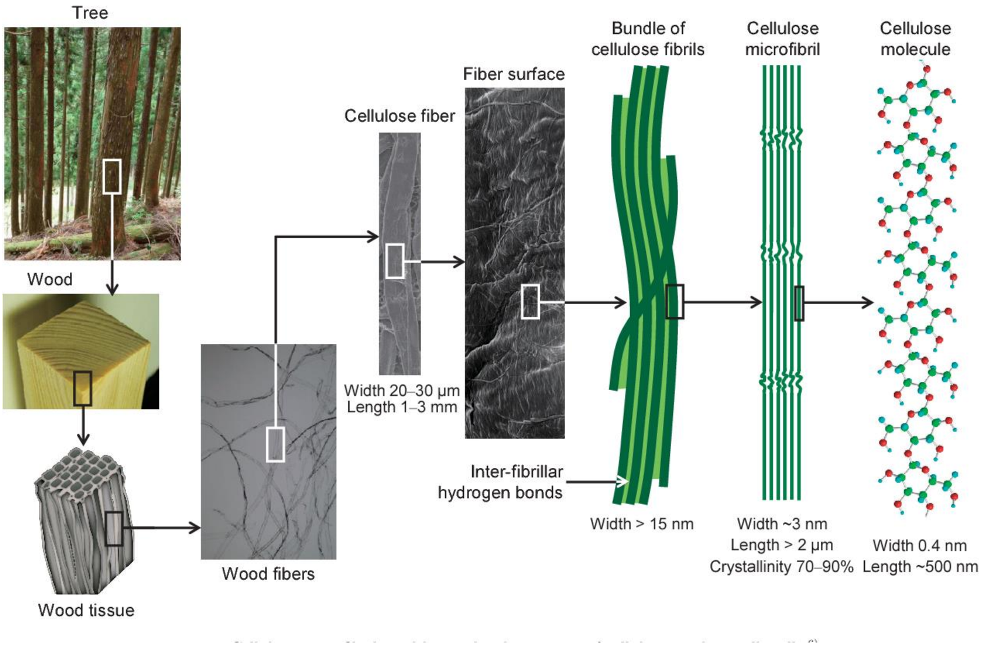


Figure 1.: The hierarchical structure of wood. Adapted from A. Isogai, T. Saito and H. Fukuzumi, Nanoscale, 3, 71–85, 2011.

To produce the CNF solution, CNF-gel was diluted (1:20 wt%) by adding ultra-purified water, after, mixed thoroughly using a mechanical mixer (12000 rpm for 10 min) and sonication (10 min). The diluted suspensions were then centrifuged (5000 rpm for 60 min) for the removal of precipitates and the supernatants.[2]

2.2. CNF freestanding films

Before starting the experiments, square shape frames were made using a polymer material, with dimensions of 1 cm^2 and 2 cm^2, and with a height of 2 mm. The frames (Figure 2) were used in all the experiments to produce films of equal size.

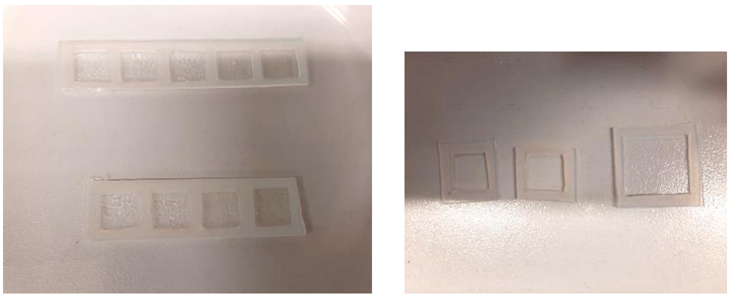


Figure 2.: Photograph of the square shaped frames used during the experiments.

2.2.1. Gel Method

This method consists in filling the frame with pure CNF-gel, using a razor to make a uniform distribution, and letting it dry. Two different types of CNF-gel were used in this project, one with a surface charge density of 400 μmol/g and the other with 1000 μmol/g.

The drying time depends on where the sample is stored. In a closed room it is necessary around 24 hours and in a room with sunlight it is necessary around 12 hours at a room temperature of 21°C. Figure 3 shows how the CNF-gel was stored during the drying process.

Figure 3.: CNF-gel storage location while drying process.

2.2.2. Dropping Method

In this method, a Pasteur pipette was used to drop the CNF solution inside the frames with the heater on. Each time the frame was filled counted as one layer. The appearance of the filled frame is shown in Figure 4. Different tests were done by changing the heater temperature, substrate material, and number of layers.

Figure 4.: Experimental setup and appearance of the filled frame.

2.2.3. Spray Method

Sprays is a process where a liquid is is blown or driven through the air in the form of tiny drops. As a deposition technique, spraying is widely applied in industry, as it is possible to produce large-scale homogeneous films, and also in laboratories for research and development.[2]

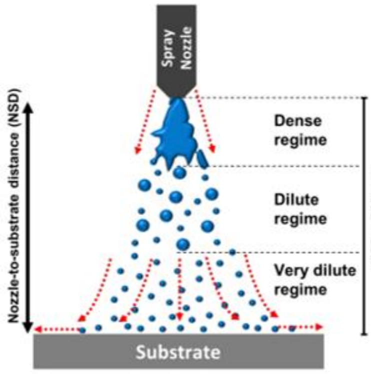


Figure 5.: Schematic of the spray or atomization process.[2]

The static spray device is a custom spray setup situated at the beamline P03 at DESY. The sample-to-nozzle distance can be adjusted, but in general this distance was kept at 200 mm in this project. The spray device has three connectors, the gas supply, the opening-cylinder and the sample feed. Any gas can be used for gas supply, although in this project only nitrogen was used due to its inertness and availability.

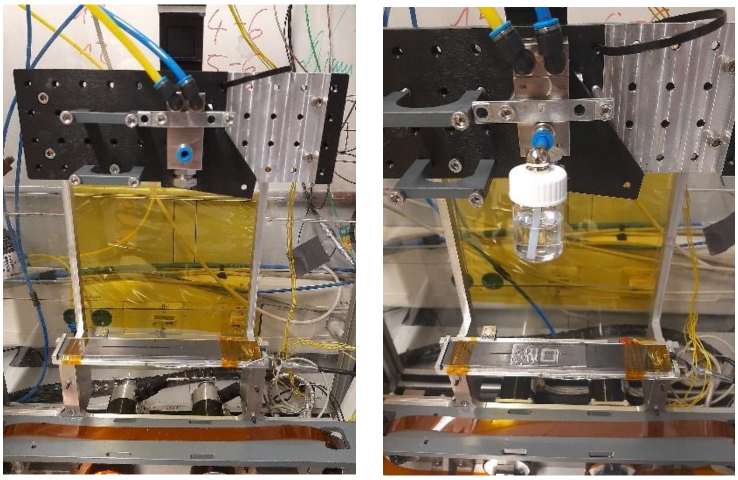


Figure 6.: Spray setup used at the synchrotron beamline P03 at DESY.[2]

- Standard Spray Parameters

During the first attempts to spray the CNF solution in the frames our standard spray parameters, which are a spray time of 0.2 seconds and a dry time of 10 seconds, were used. The number of spray pulses was adapted for specific tests. Different substrates were used (silicon wafers and PTFE (Teflon)), to test which of the substrates would be easier to remove the CNF film (Figure 7).

Figure 7.: Photos of the used substrate materials: Silicon wafer (left image) and Teflon (right image).

- Dropping Parameters

As a second test, the same principles of the dropping method were repeated using the spray setup. Some tests were made to find out how much spray would be necessary to fill the frame, as well as the drying time, and the best sample-to-nozzle distance.

2.3. Removal of CNF-films from substrates

To remove the CNF films from the substrates, two methods were used. The first is to remove the film without solvent, only in air, using tweezers and pulling the edges of the film carefully in order not to tear it. The second method was to, put the substrate with the CNF film on it into a vessel with water for a certain amount of time and using a steel spatula to remove the CNF film. The second method was used in case that method one was not possible.

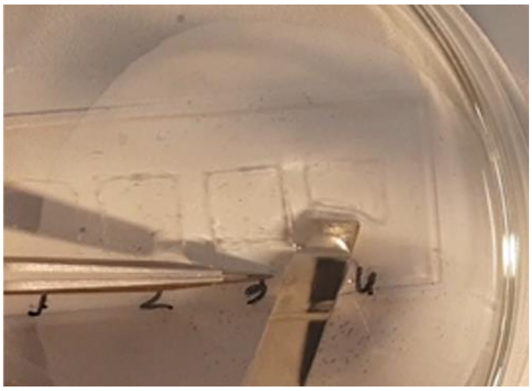


Figure 8.: Photo of a film being removed in water.

2.4. Silver Nanowires

Silver nanowires (AgNWs) combine high electrical conductivity with low light extinction in the visible light range, and are used in a wide range of applications: in the field of electronics, optics, acoustics, magnetics and high-performance catalysts.[4] The CNF films were functionalized with AgNWs by spraying two different kinds of AgNWs- inks using the standard spray parameters cited above (chapter 2.2.3).

Type I) AgNW diluted in Isopropanol

Type II) a mixture of AgNW and aqueous CNF solution

To produce the ink, AgNWs were diluted with the corresponding solvent, to the desired concentration. After that, the AgNW-dispersions were put into the ultra-sonic bath for 2 min. The concentrations used was 1:10 and 2:10 by volumne.

- CNF-gel

CNF gel (400/1000 µmol/g) was put into frames, as explained above (chapter 2.2.1), and then the AgNW ink (type I and II), with the two different concentrations, was sprayed on top of the wet gel. The number of sprays pulses were 12, 15 and 18 times. The films were left to dry overnight and on the next day the films were removed from the substrate and their conductivity was measured.

Also, using the CNF-gel films already prepared (dry), AgNW ink (type I and II - concentration 1:10) was sprayed using standard parameters on the top of the films and their conductivity was measured.

- CNF-spray film

The best films produced using the spray method were functionalized using the AgNW ink (type I and II - concentration 1:10) and the conductivity of the films were measured.

2.5. Analysis of CNF-films

- Solvent Tests

The CNF-gel films were put inside nine different solvents to test their resistance and solubility. The following solvents were used: Distilled water, Acetone, Isopropyl, Ethanol, Toluene, Chloroform, Chlorobenzene, 2-MTHF and Ethyl lactase.

The following method was used: First, the CNF-films were put in the different solvents for 20-30 seconds, 5 minutes, and 3 hours. After that, the films were removed, and their properties were checked.

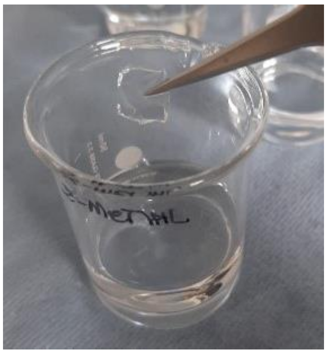


Figure 9.: Photo representing the solvent test process.

- Microscopy

An optical microscope creates a magnified image of an object specimen with an objective lens and magnifies the image further more with an eyepiece to allow the user to observe it by the naked eye. The surface and the thickness of the CNF-films was measured using the optical microscope (VH-Z250R, Keyence, Japan).

- Transmission

The light transmission of the CNF-films was measured in the wavelength range of 200 to 900 nm using an ellipsometer (ESM-300, J.A. Woollam Co., US). Ellipsometry measures a change in polarization as light transmits from a material structure in comparison to air. The wavelength used to compare the transparency of the films was 550 nm.

- Conductivity (four-point probe)

The conductivity of the films functionalized with AgNW were measured using a Four-Point Probe System (Four-Point Probe, Ossila, UK), which the purpose is to measure the resistivity of any semiconductor material. This measurement uses four probes arrayed in a line, with equal spacing between each probe. A current is passed between the outer two probes, causing a reduction in voltage between the inner two probes, by measuring this change in voltage, the sheet resistance can then be calculated.

3. Results and Discussion

3.1. CNF freestanding films

3.1.1. CNF-gel films

The films produced by the gel method were easily removed from the frame and the glass substrate in air. Below are the images (Figure 10) of the dried CNF-gel films.

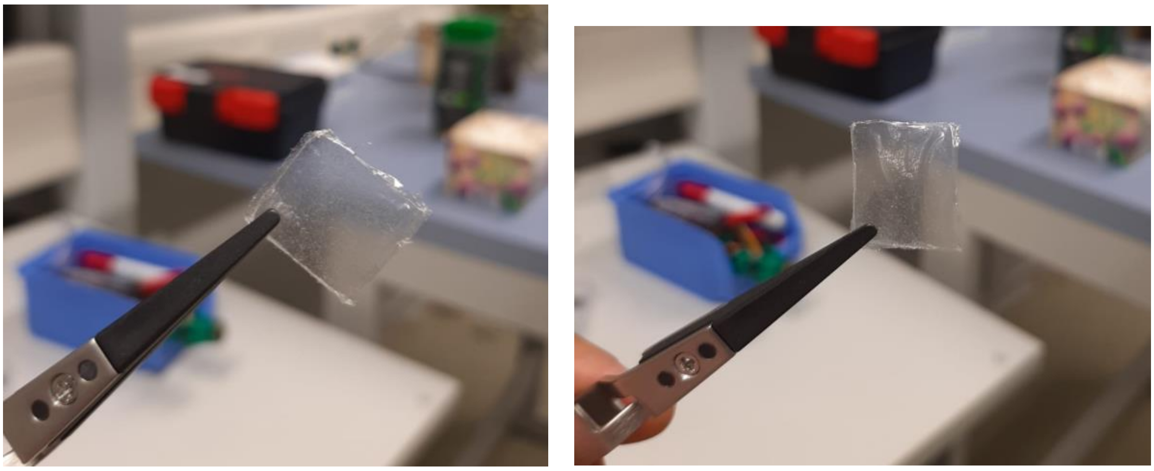


Figure 10.: Left image shows the CNF-gel 1000, and on the right is the CNF-gel 400.

To find out how much light went through the film, the light transmission data was measured. Figure 11 shows the transmission of the CNF-gel-films with a loading of 400 µmol/g and 1000 µmol/g. Between 200 nm up to 750 nm the CNF-gel film 400 has a lower transmission than the CNF-gel film 1000. However, for wavelength < 750 nm, the CNF-gel-film 1000 is less transparent.

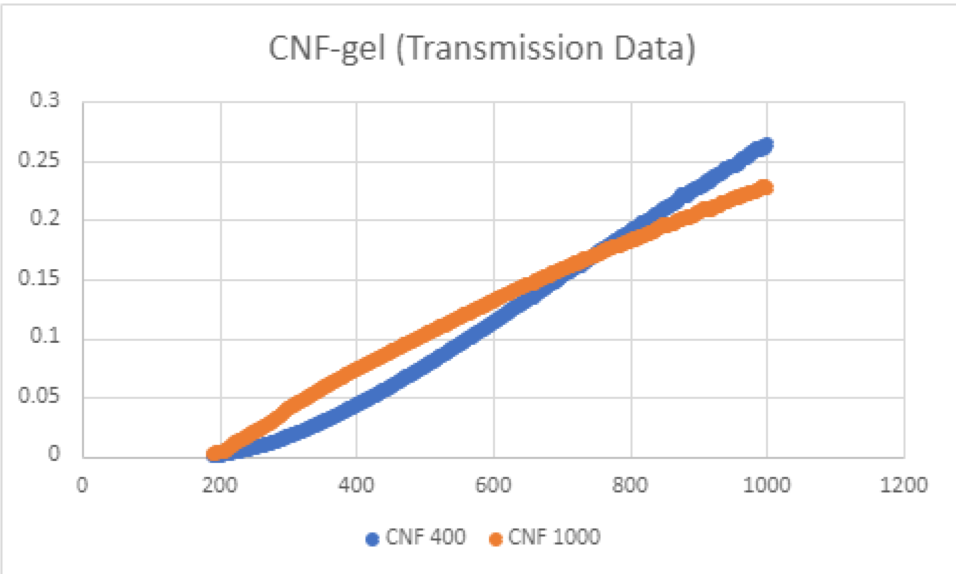
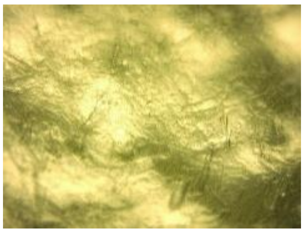
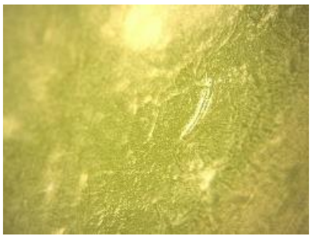


Figure 11.: Transmission data of CFN-gel films.

The thickness of the CNF-films was measured using the optical microscope. Both films show a similar thickness (see Table 1.) Furthermore, the surface of the CNF-gel 400 film appears less rough to the eye than the surface of the CNF-gel 1000.

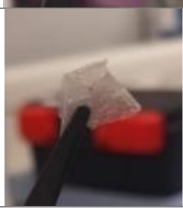
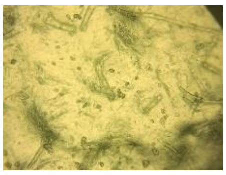
Table 1.: Data from CNF-gel films produced.

Results CNF – gel films				
Type	**Photo of the film**	**Photo surface**	**Thickness (um)**	**Transmission (at 550 nm)**
CNF 1000			2.248	12.66%
CNF 400			2.255	9.17%

- Solvent stability tests

None of the tested solvents affected the CNF-films strongly, none of them was capable of dissolving the CNF-film structure again. Tensile strength and flexibility tests were performed manually on the films. As some of the tests showed opposite results when the films with different charges (400 and 1000 µmol/g) were put in the same solvent, the experiment was done a second time, to check the results. The data and analyses are shown in the tables below (Table 2, 3).

Table 2.: Data from CNF-gel film 1000 when put inside different solvents.

CNF- gel film 1000 in different solvents					
Solvent	**Appearance First test**	**Appearance Second test**	**Photo**	**Photo surface**	**Transmission (at 550 nm)**
Chloroform	Medium resistance; flexible	Low resistance; flexible			8.56%
Isopropanol	Low resistance; low flexibility	Low resistance; flexible			7.93%

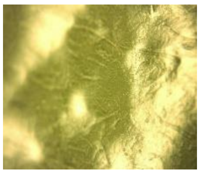
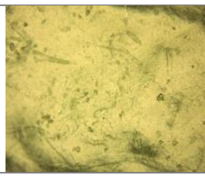
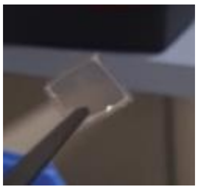
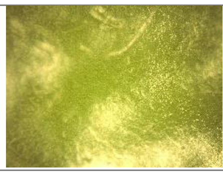
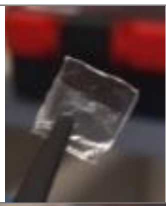
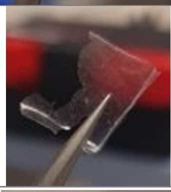
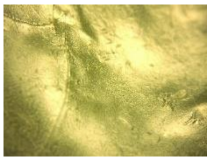
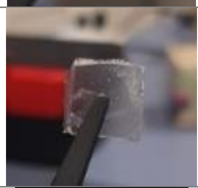
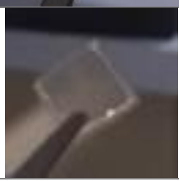
2-MTHF	Medium resistance; medium flexibility	Medium resistance; flexible			7.55%
Toluene	Medium resistance; flexible	-			8.56%
Chlorobenzene	Not possible to see it, it stuck in the sample box	Medium resistance; flexible			9.46%
Acetone	It breaks very easily; low resistance	Medium resistance and flexible			11.38%
Ethanol	Good resistance; flexible	-			9.31%
Water	Good resistance; flexible	-			7.28%
Ethyl lactase	Low resistance, it breaks easily	-			-

Table 3.: Data from CNF-gel film 400 when put inside different solvents.

CNF- gel film 400 in different solvents					
Solvent	**Appearance First test**	**Appearance Second test**	**Photo**	**Photo surface**	**Transmission (at 550 nm)**
Chloroform	Low resistance; flexible	Good resistance; flexible			10.42%

Isopropanol	Good resistance; flexible	Good resistance; flexible			8.25%
2- MTHF	Fragile; low resistance; low flexibility	Good resistance; flexible			10.96%
Toluene	Medium resistance; medium flexibility				7.44%
Chlorobenzene	Good resistance; flexible	Good resistance; flexible			8.89%
Acetone	Good resistance; flexible	Good resistance; flexible			10.46%
Ethanol	Good strength; flexible				8.18%
Water	Good strength; flexible				7.65%
Ethyl lactase	Low resistance				-

For CNF gel 1000, acetone had almost no effect on the light transmittance., On the other hand, water had the strongest effect on the transmittance of the film, being 5% less transparent than the original film. However, , for the CNF gel 400 films, some of the solvents, such as acetone and 2- MTHF, made the film more transparent, while water again affected the quality of the films the most.

Therefore, considering all the data, the CNF-gel 400 presented better results than the CNF-gel 1000: They are more solvent-resistant and flexible. Thus, all following experiments were done using the CNF solution 400.

Another interesting observation is that when the CNF-gel is put in water and taken out after 5 minutes it presents an interesting effect, as shown in the images (Figure 12) below. The film crumples and immediately one part sticks to the other. However, after 3 hours inside the water, this effect is not noticeable anymore.

Figure 12.: Photos of one part of the film sticks to the other

3.1.2. CNF-drop films

CNF-films were prepared using the dropping-technique described before (chapter 2.2.2.). A temperature of 75 °C was used to increase the rate of evaporation. However, it was noticed that this temperature was not good for the CNF film properties since the solution was boiling. Thus, there were a lot of bubbles in the final films, which reduced its quality (see Figure 13).

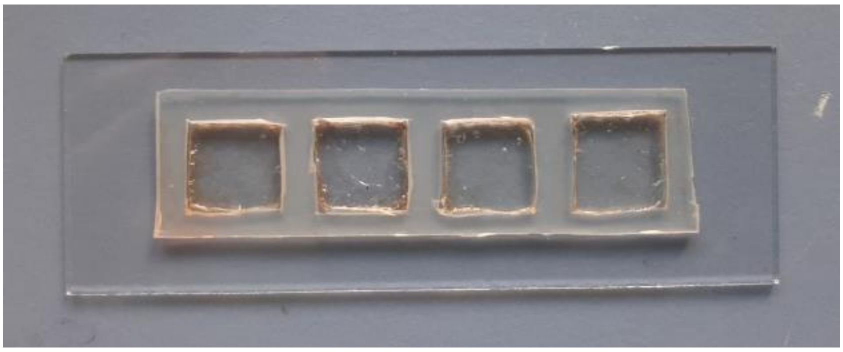


Figure 13.: Photos of one part of the film sticks to the other.

Hence, for the following experiments, the temperature was reduced to 45 °C. But even at this temperature, some air bubbles were formed. Attempts were made to remove them using a needle, but some bubbles still remained.

However, it was possible to make free-standing films using the dropping-technique. Using the CNF solution 400 (1:20) and 10 layers on glass, the film of the image below was made. It was pulled off the glass substrate by putting it in water.

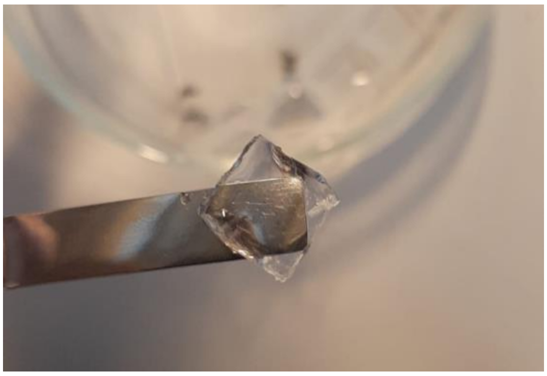


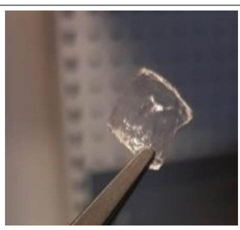
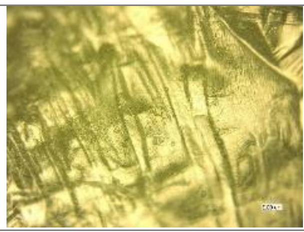
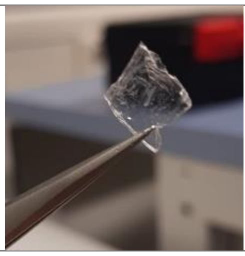
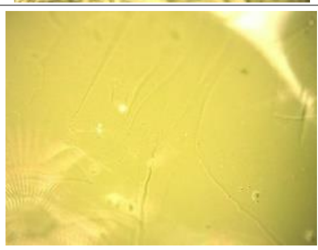
Figure 14.: Photos of the film made using the dropping-technique.

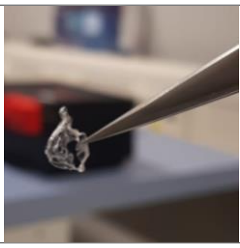
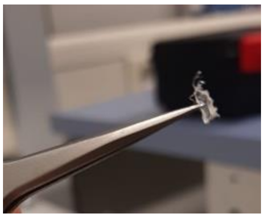
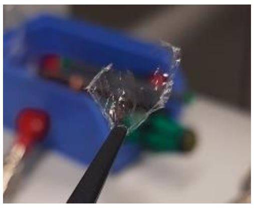
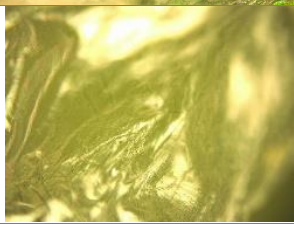
Also, instead of glass, Teflon was used as substrate material. It was possible to produce a great film dropping the CNF solution 3 times (layers) into the frame. It was also easy to pull it off from the Teflon surface and it was possible to remove it using the first removal method just in air.

Figure 15.: Photos of the film made using the dropping-technique in Teflon

In the table below are some data of the films produced.

Table 4.: Data from CNF-drop film 400.

Results CNF – drop films 400 (1:20)			
Type	**Photo Film**	**Photo surface**	**Thickness (um)**
10x			5.150
8x			3.580

5x			2.799
3x			2.142
3x (TEFLON)			1.879

3.1.3. CNF-Spray films

3.1.3.1. Standard Parameters

- Silicon wafers

The CNF solution 400 (1:20) was sprayed in frames using the standard parameters and the number of spray pulses was 20, 50 and 100 pulses. Below are the images of the silicon wafers after spraying (Figure 17).

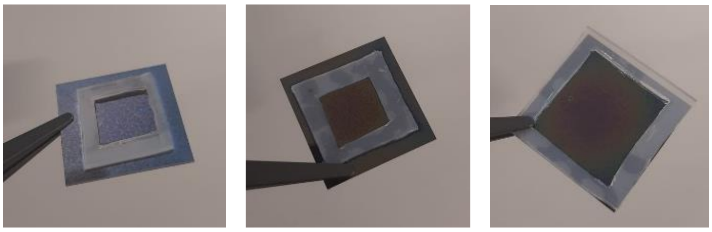


Figure 17.: Photos of the silicon wafers sprayed with CNF solution.

It was not possible to take off a film of CNF, even letting it inside water for 3 hours, because the CNF-layer was too thin. Below are the images (Figure 18) of the tiny pieces of CNF that were possible to take off.

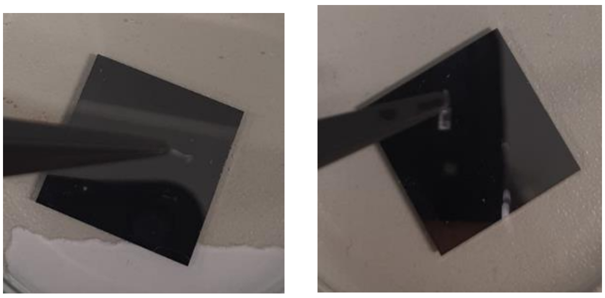


Figure 18.: The first photo shows 20 spray pulses (p), and the second shows 100p.

- Teflon

Using the standard parameters and 300 spray pulses it was possible to take off a CNF film from the TEFLON. The film was fragile and tore easily.

Figure 19.: CNF film made using the standard parameters and Teflon as surface.

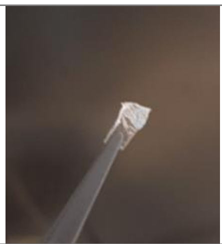
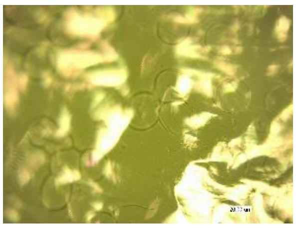
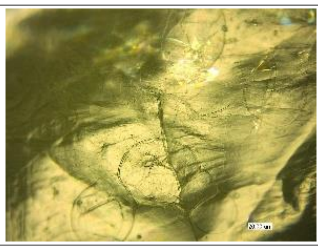
3.1.3.2. Dropping Parameters

The CNF solution 400 (1:20) was sprayed in Teflon and glass trying to reproduce the results of the dropping method.

- Teflon

The parameters of spraying were: 8 seconds of spray, 600 seconds to dry, 5 and 10 pulses, at 100°C. The 10 pulses film was possible to remove just in air, but the 5p was removed using water.

Table 5.: Data from CNF-spray film 400 in Teflon.

Results CNF – spray films 400 (1:20) - Teflon			
Type	**Photo Film**	**Photo surface**	**Thickness (um)**
5p			3.020
10p			5.109

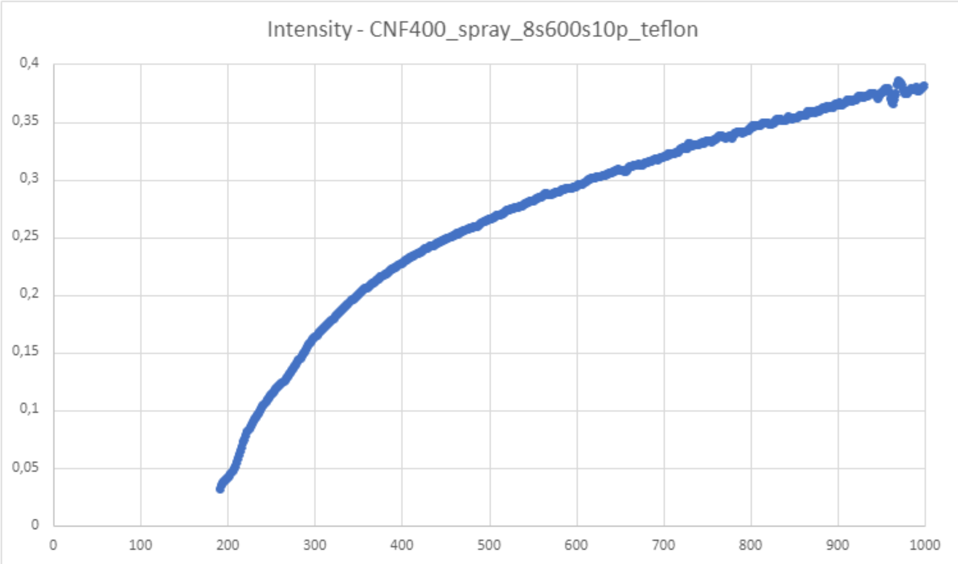


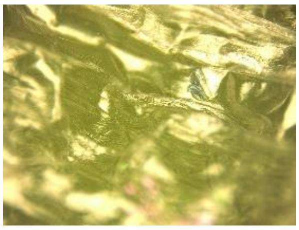
Figure 20.: The light transmission data of the CNF-film sprayed on Teflon using 10 pulses.

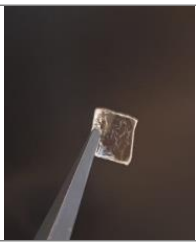
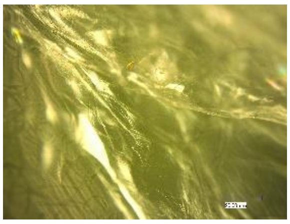
In summary, Teflon is an excellent substrate material, as it is possible to produce free-CNF films with fewer layers, and therefore the films are also thinner than these fabricated using other substrate materials. However, the production of Teflon is not ecologically sustainable, presenting several risks to the environment, which goes against the whole concept of this research. Therefore, even though it presents good results, the project was continued using glass as a surface, since it presented the best results after Teflon and is a more sustainable and recyclable material.

- Glass slides

The first attempt using glass as a surface was spraying the CNF solution 400 (1:20) with the following parameters: 8s of spray, 420s to dry, and the number of spray pulses of 10, 12 and 15 at 100°C. It was possible to remove all the films in water.

Table 6.: Data from CNF-spray film 400 in glass.

Results CNF – spray films 400 (1:20) - glass			
Type	**Photo Film**	**Photo surface**	**Thickness (um)**
10p			2.640
12p			3.570

15p			4.655

The solvent test results proved that water makes the film less transparent, so it is important to avoid using water to remove films from the substrate. Therefore, to discover how many layers are necessary to take off the films sprayed on the glass without water, the CNF solution was sprayed using the same parameters, but with 30 spray pulses. It was possible to remove the films in air easily, photos of the films are below (Figure 21.).

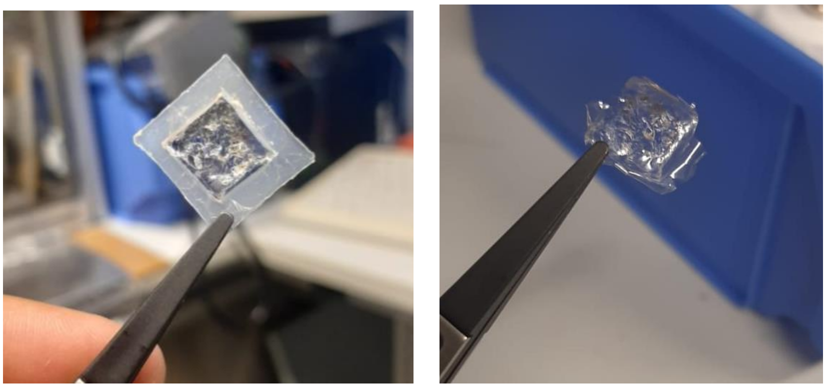


Figure 21.: CNF-film sprayed using dropping parameters and 30 pulses.

In this film, several bubbles were formed and some parts of the film had burned appearance. Thus, the temperature of the heater was decreased to 45°C for the next experiments. At this temperature the dry time was longer, but there was not much bubble formation and the film looked better.

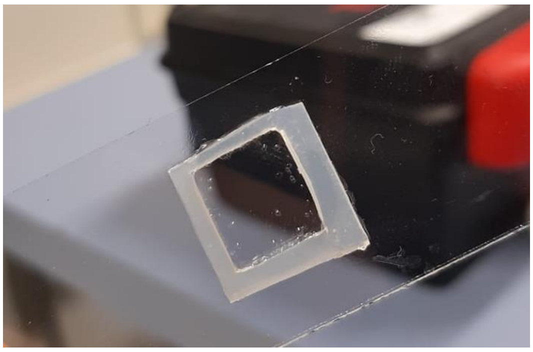


Figure 22.: CNF-film sprayed using dropping parameters and 10 pulses at 45°C

Thus, another test was done using the following parameters: 8 seconds of spray, 1500 seconds of dry time and 35 pulses. It was possible to remove it without water and the quality of the film was great (Figure 23.).

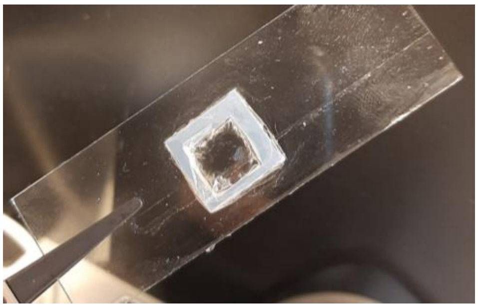
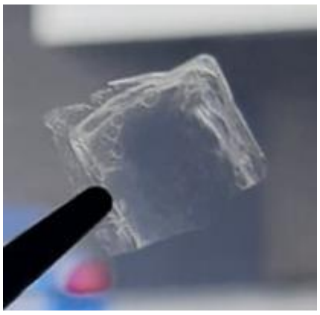
 

Figure 23.: CNF-film sprayed using dropping parameters and 35 pulses at 45°C

The surface photo made using the microscope is shown in Figure 24, and the thickness of the film was approximately 2.950 µm.

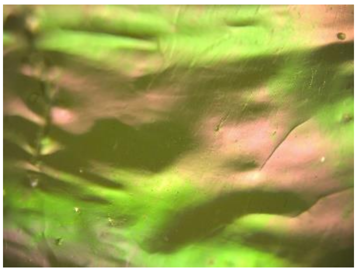


Figure 24.: Surface photo of CNF-film sprayed using dropping parameters and 35 pulses at 45°C

The transmission of the film was also measured, Figure 25, and presented a great result.

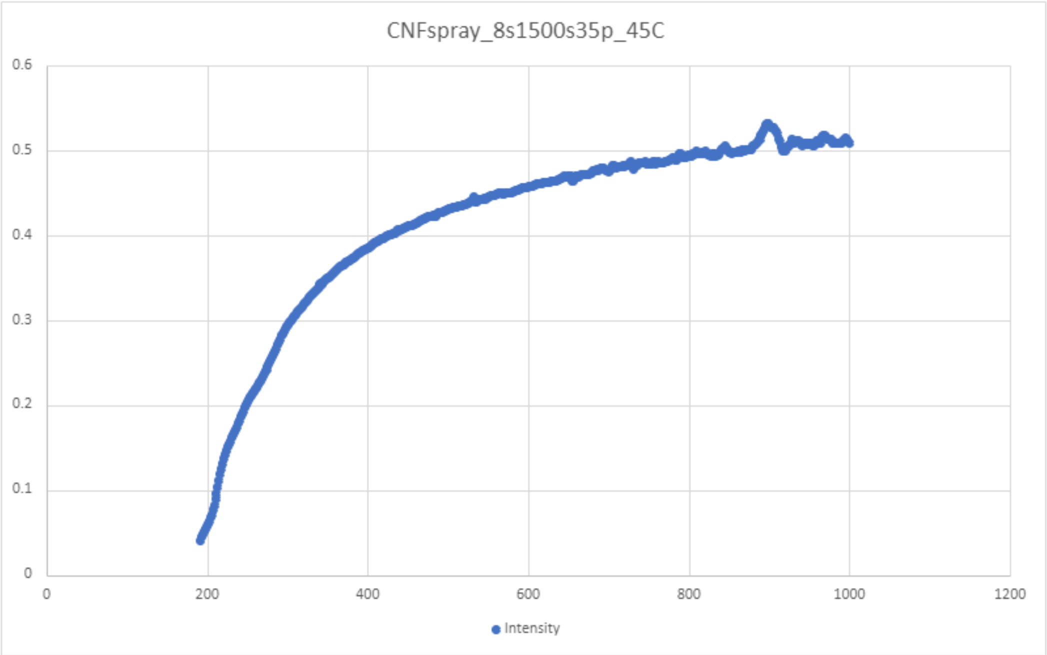


Figure 25.: Light transmission of CNF-film sprayed using dropping parameters and 35 pulses at 45°C

The spraying method, using the parameters cited above, produced the best film so far. However, CNF solution spending is very high. To produce a 1x1 cm² film it is necessary to spray approximately 45 mL of solution. This is because some amount of the solution also spreads over the whole substrate (Figure 26.).

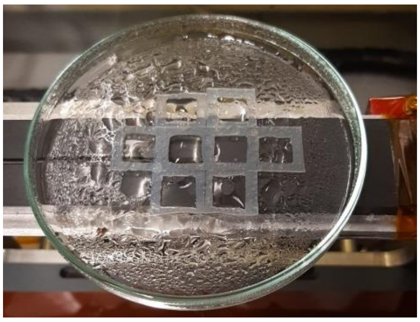


Figure 26.: Photo of the amount of solution that spreads due to the focus of the nozzle

Thus, not everything that is sprayed stays inside the frame. To improve the efficiency of the process, the height of the nozzle was decreased, from 20 cm to 14 cm. That way it was possible to fill 4 frames with the same amount of solution used to fill just 2 frames at 20 cm.

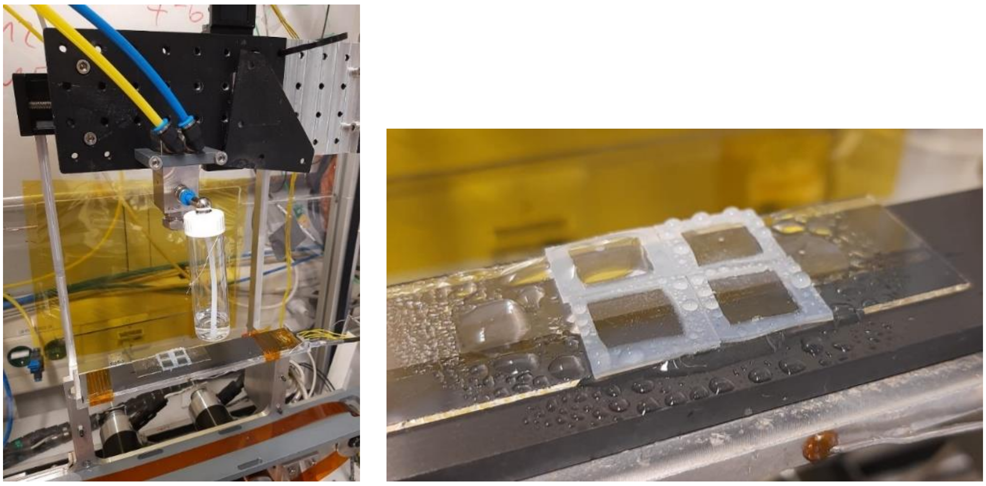


Figure 27.: Photo of the spray setup and the frames filled with CNF solution.

As it had more frames, the dry time increased, being equal to 1700 seconds. The films were taken off the glass, it was not difficult to remove them in air.

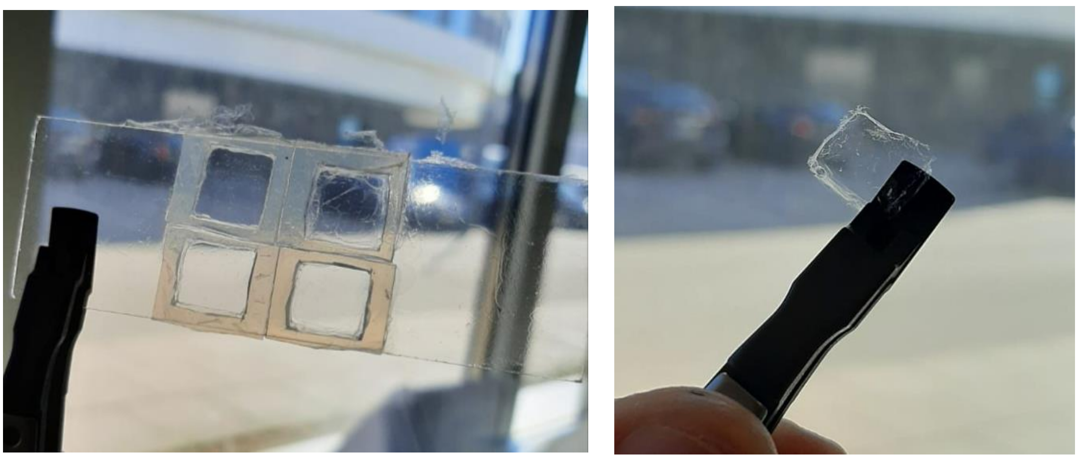


Figure 28.: Photo of the CNF films produced.

The surface photo made using the microscope is below (Figure 29.) and the thickness of the film was approximately 3.29 µm.

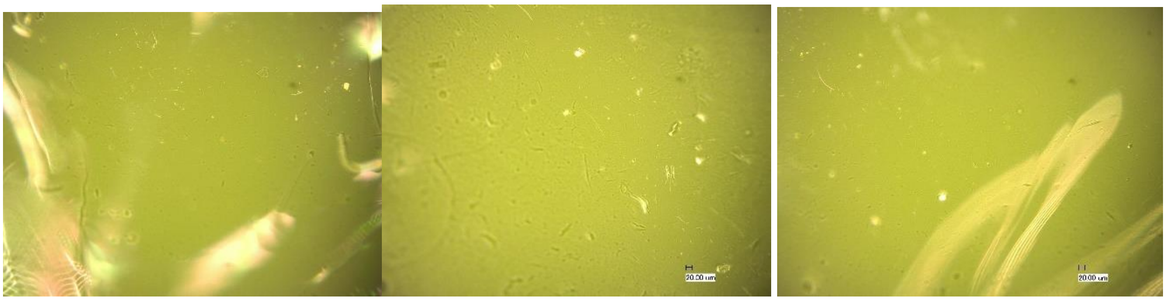


Figure 29.: Surface photo of the CNF films produced.

The transmission of the films was measured. In the graphic below (Figure 30.) are the average light transmission data of the films produced. The light transmission at 550 nm is 79.43 %.

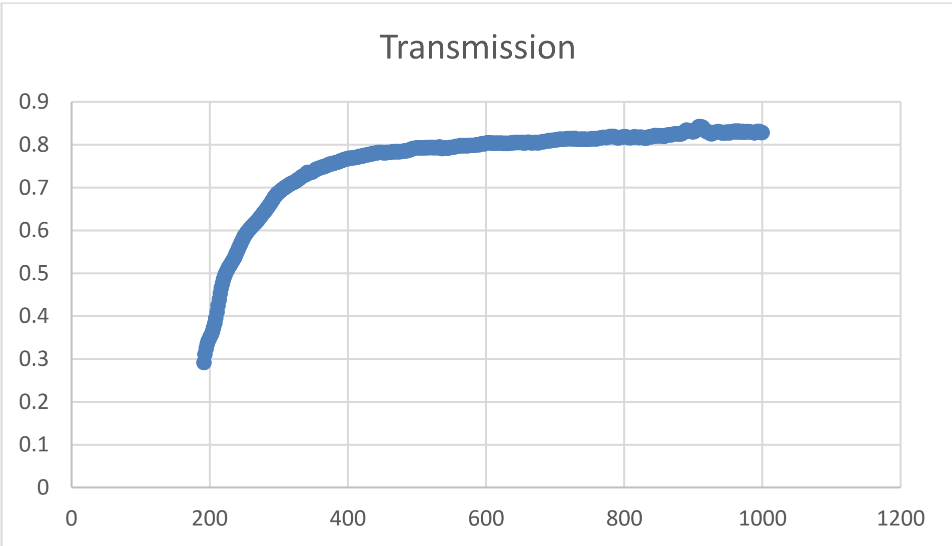
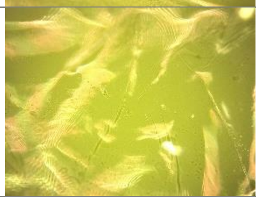
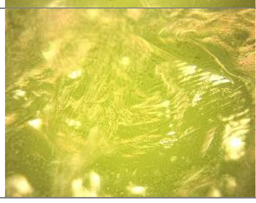


Figure 30.: Light transmission of the CNF films produced.

This is the best spray-film produced in this project, therefore, a solvent test was made with these films to see how they would react. Even after 3 hours inside the solvents, the films were still intact.

Table 7.: Data from best CNF-spray film 400 in different solvents.

CNF-spray film in different solvents		
Solvent	**Photo surface**	**Transmission (at 550nnm)**

Chloroform		26.99%
Isopropanol		37.83%
2-MTHF		52.96%
Toluene		56.51%
Chlorobenzene		68.79%
Acetone		69.37%
Ethanol		52.88%
Water		36.61%

Thus, the solvents that most interfered with light transmission were water and chloroform, acetone was the one that less interfered with the light transmission.

3.2. Silver nanowires (AgNW)

- AgNWs on CNF-gel film

The films resulting from the process explained above (chapter 2.4) were taken off on air. One observation is that this process is more difficult in comparison to the normal CNF-gel films.

The sheet resistance, resistivity, and conductivity of the films were measured at 4 different positions on the film, below is the table (Table 8) with the results. It was not possible to measure the conductivity of films in which the AgNW ink type I was applied, and also, the film which was taken off using water, probably the paint was washed in this process.

Table 8.: Conductivity data from CNF-gel and AgNW ink.

CNF-gel (400) + AgNW ink (Type II) – 12 pulses			
Position	Sheet resistance (Ω^{-1})	Resistivity ($\Omega \cdot m$)	Conductivity ($S \cdot m^{-1}$)
1	$1.992 \cdot 10^{3}$	$2.988 \cdot 10^{-4}$	$9.501 \cdot 10^{3}$
2	-	-	-
3	$8.974 \cdot 10^{4}$	$1.346 \cdot 10^{-2}$	$7.438 \cdot 10^{1}$
4	-	-	-

CNF-gel (400) + AgNW ink (Type II) – 15 pulses			
	Sheet resistance (Ω^{-1})	Resistivity ($\Omega \cdot m$)	Conductivity ($S \cdot m^{-1}$)
1	205.85	$3.088 \cdot 10^{-5}$	$3.241 \cdot 10^{4}$
2	$1.683 \cdot 10^{3}$	$2.524 \cdot 10^{-4}$	$3.962 \cdot 10^{3}$
3	$4.920 \cdot 10^{3}$	$7.379 \cdot 10^{-4}$	$1.357 \cdot 10^{3}$
4	$2.337 \cdot 10^{3}$	$3.505 \cdot 10^{-4}$	$2.853 \cdot 10^{3}$

CNF-gel (400) + AgNW ink (Type II) – 18 pulses			
	Sheet resistance (Ω^{-1})	Resistivity ($\Omega \cdot m$)	Conductivity ($S \cdot m^{-1}$)
1	146.54	$2.198 \cdot 10^{-5}$	$4.549 \cdot 10^{4}$
2	734.59	$1.102 \cdot 10^{-4}$	$9.094 \cdot 10^{3}$
3	$3.164 \cdot 10^{3}$	$4.746 \cdot 10^{-4}$	$2.109 \cdot 10^{3}$
4	$4.217 \cdot 10^{3}$	-	-

CNF-gel(1000) + AgNW ink (Type II) - 12p			
	Sheet resistance (Ω^{-1})	Resistivity ($\Omega \cdot m$)	Conductivity ($S \cdot m^{-1}$)
1	$3.765 \cdot 10^{4}$	$5.648 \cdot 10^{-3}$	$2.655 \cdot 10^{2}$
2	$7.197 \cdot 10^{4}$	$1.080 \cdot 10^{-2}$	$9.281 \cdot 10^{1}$
3	$5.623 \cdot 10^{4}$	$8.435 \cdot 10^{-3}$	$1.187 \cdot 10^{2}$
4	$2.863 \cdot 10^{6}$	$4.294 \cdot 10^{-1}$	$2.607 \cdot 10^{2}$

CNF-gel(1000) + AgNW ink (Type II) - 15p			
	Sheet resistance (Ω^{-1})	Resistivity ($\Omega \cdot m$)	Conductivity ($S \cdot m^{-1}$)
1	$8.242 \cdot 10^{3}$	$1.236 \cdot 10^{-3}$	$8.096 \cdot 10^{2}$
2	-	-	-
3	$9.481 \cdot 10^{4}$	$1.422 \cdot 10^{-2}$	$7.042 \cdot 10^{1}$
4	$2.531 \cdot 10^{3}$	$3.797 \cdot 10^{-4}$	$2.723 \cdot 10^{3}$

Below are some photos of the surface of the films in the microscope.

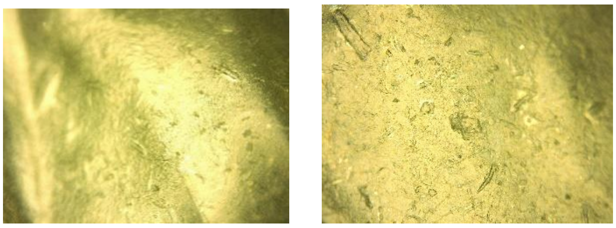


Figure 31.: Surface of CNF-gel film (400) sprayed with AgNW ink type I (right) and type II (left).

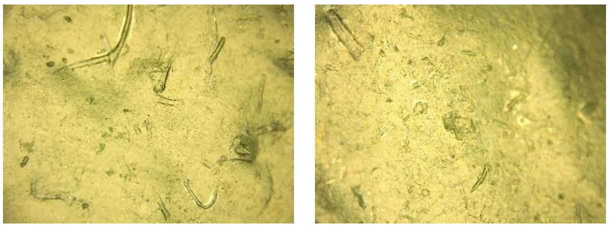


Figure 31.: Surface of CNF-gel film (1000) sprayed with AgNW ink type I (right) and type II (left).

The films of CNF-gel sprayed with the higher concentrated ink (2:10) were taken off the frames and their conductivity were measured (Table 9).

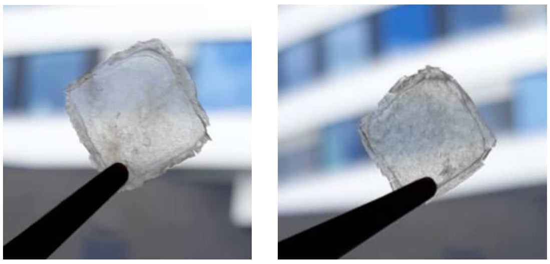


Figure 32: Photo of the CNF-gel 400 films after 15p (right) and 18p (left) of AgNW ink (type II).

Table 9.: Conductivity data from CNF-gel and AgNW ink – Comparation concentration 1:10 and 2:10.

Position	CNF-gel(400) + AgNW ink (Type II) (1:10) - 15p	CNF-gel(400) + AgNW ink (Type II) (2:10) - 15p
	Sheet resistance (Ω^{-1})	Sheet resistance $(\Omega/square)$
1	205.85	261.2
2	$1.683 \cdot 10^3$	43.19
3	$4.920 \cdot 10^3$	89.47
4	$2.337 \cdot 10^3$	64.8

Position	CNF-gel(400) & + AgNW ink (Type II) (1:10) - 18p	CNF-gel(400) + AgNW ink (Type II) (2:10) - 18p
	Sheet resistance (Ω^{-1})	Sheet resistance $(\Omega/square)$
1	146.54	9.805
2	734.59	18.47

3	$3.164 \cdot 10^3$	8.401
4	$4.217 \cdot 10^3$	16.27

As expected, the sheet resistance decreased when a AgNW ink with a higher concentration was applied. The light transmission of the films was measured and below are some of the results.

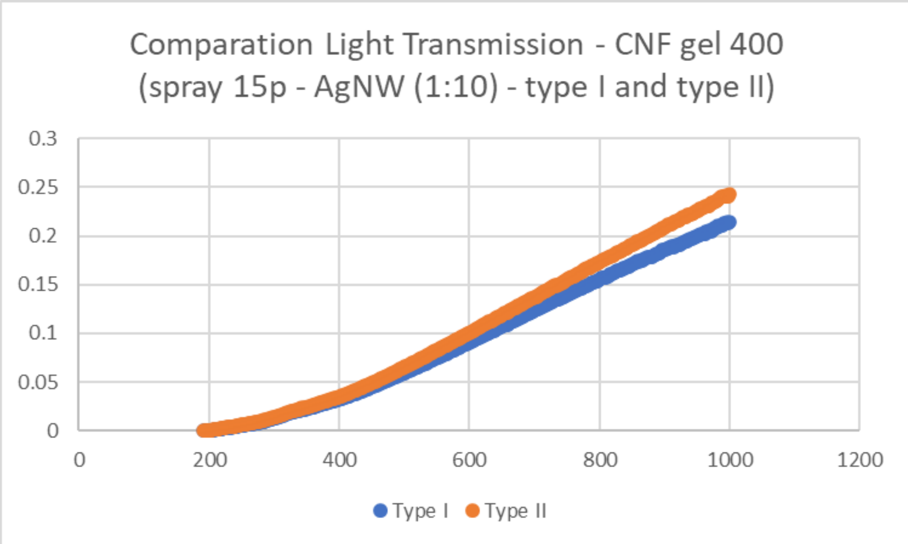


Figure 33: Light transmission data from CNF-gel (400) with AgNW ink (type I and type II II - concentration 1:10).

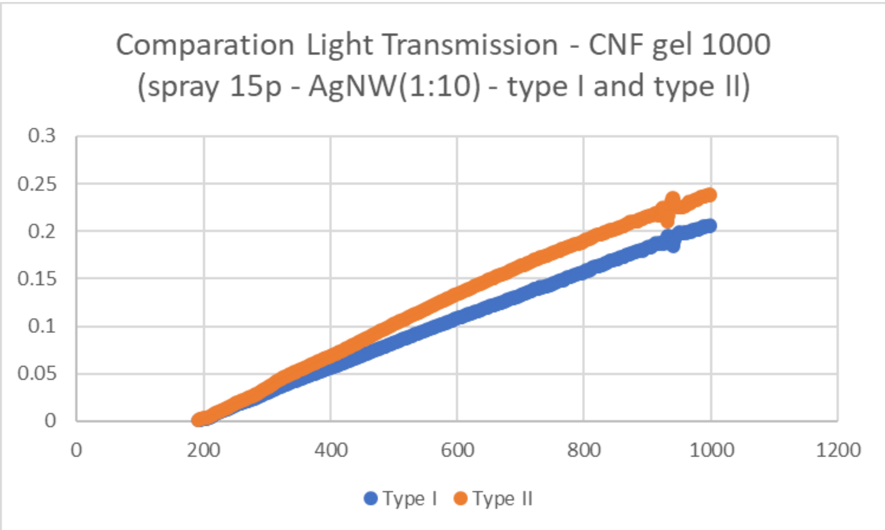


Figure 34: Light transmission data from CNF-gel (1000) with AgNW ink (type I and type II - concentration 1:10).

Therefore, the AgNW ink (type I) interferes less with the transparency of the film. And, as it is possible to see in the graphic below (Figure 35), the transparency of the films decreases proportionally with the number of ink layers applied.

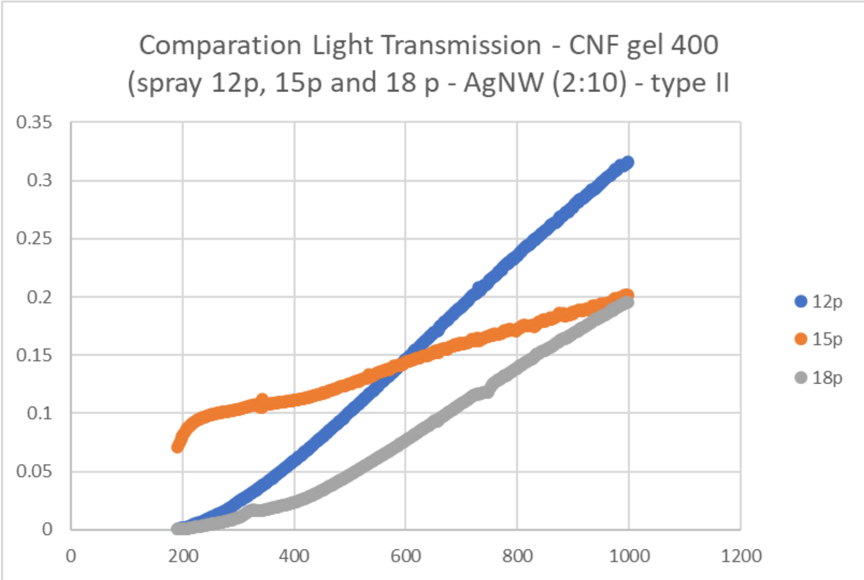


Figure 35: Light transmission data from CNF-gel (400) with AgNW ink (type II - concentration 2:10).

Another test done was to use the freestanding CNF gel films (400) already prepared and spray the AgNW ink (type I and II), using 15 and 18 pulses. It was only possible to measure the conductivity from the one sprayed 18 times using the AgNW ink type II, it had a sheet resistance of $9.015 * 10^4 \Omega^{-1}$.

- CNF-spray film

The best film produced using the spray method was the chosen one to be sprayed with AgNW ink. Thus, the test was done using the 2 types of AgNW ink and the standard spray parameters, with 15 pulses. The surface photos of the films are below (Figure 36).

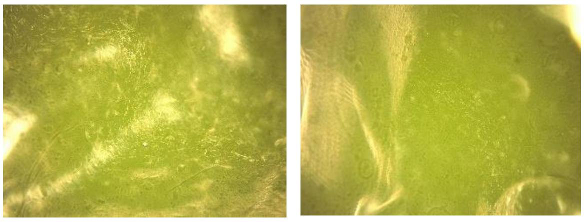


Figure 36.: Microscopy image of best sprayed CNF films with AgNW ink Type I (left) and Type II (right) on top.

It was only possible to measure the conductivity from the one sprayed 18 times using the AgNW ink type II, it had a sheet resistance of $10.94\ \mathrm{M\Omega/square}$. The light transmission was measured (Figure 37). At a wavelength of 550 nm, the film sprayed with type I had a transmission of 54 % and the one sprayed with type II had a transmission of 50 %.

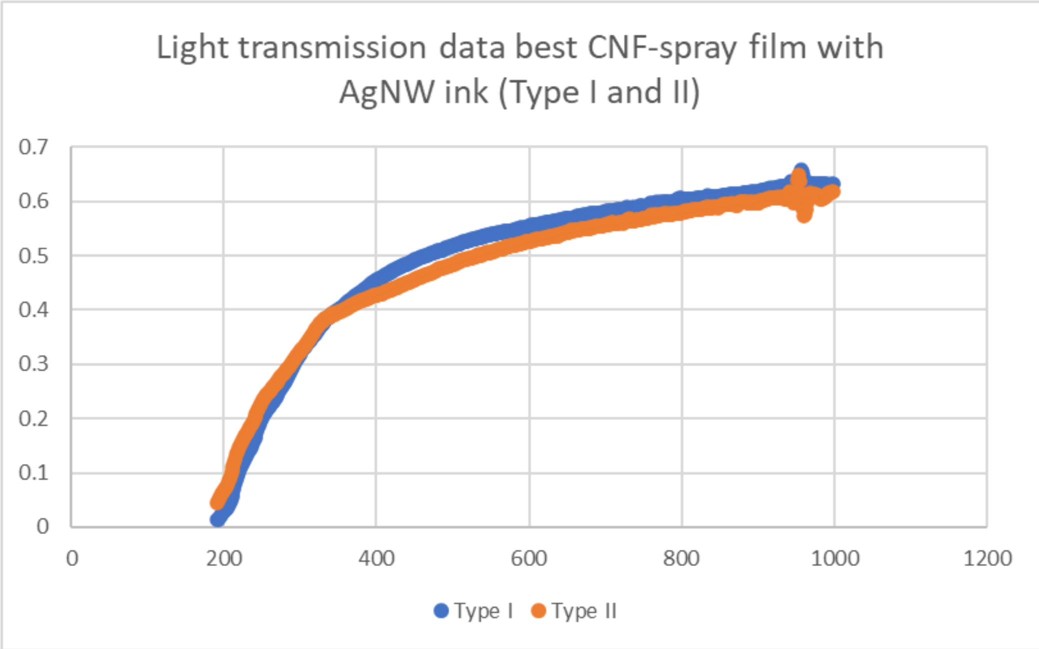


Figure 37.: Light transmission data best CNF-spray film with AgNW ink (Type I and II).

Compared to the original film the transparency has decreased by approximately 30 %, but it is still the CNF-film that has the highest light transmission of all tested films.

4. Conclusions & Outlook

To produce freestanding CNF films, three different methods were used: gel, drop casting, and spraying. Furthermore, CNF gel and solution with different surface charges, as well as different substrate materials were tested. The electronic properties and structure of the most promising samples were investigated using solvent tests, microscopy, ellipsometer and four-point measurements.

With the results of the tests performed using Teflon as a substrate, it can be seen that it is an excellent substrate material, as it is possible to produce free-CNF films with fewer layers, and therefore the films are also thinner than these fabricated using other substrate materials. However, the production of Teflon is not ecologically sustainable, presenting several risks to the environment, which goes against the whole concept of this research. Therefore, the best substrate after Teflon is glass, since it was possible to produce good films and it is a more sustainable and recyclable material.

The best film produced was made using the spray-method and glass as substrate material. The spray parameters were: 8 s spraying, 1700 s waiting and 35 pulses at a temperature of 45 °C. This film showed excellent properties of tensile strength, flexibility and transparency (79.43 % light transmission at 550nm, $10.94\ \mathrm{M\Omega/square}$).

In the solvent tests, the solvent that interfered less with the transparency of the films was acetone, and the one that made the film less transparent was water, which for example caused an decrease of the light transmission of the best film to 36,61%. The solvent test results prove, that water makes the film less transparent, so it is important to avoid using water to remove films from the substrate.

Three kinds of CNF films were functionalized with AgNWs, spraying the two different types of ink with two different concentrations. None of the films sprayed with AgNW ink type I were conductive. As expected, the sheet resistance decreased with increasing ink concentration. The film which had the smallest sheet resistance, thus is more conductive, was the CNF-gel 400 (wet) sprayed with 18 pulses of AgNW ink (Type II – concentration 2:10), with an average sheet resistance of 13.24 $\Omega/square$. The light transmission of the best spray-film decreased to 50% when AgNW ink type II was applied, but it is still the CNF-film that has the highest light transmission.

The next generation of microelectronics is aiming for applications of "electronics everywhere," and such organic semiconductors will play a major role in these future technologies. Therefore, our findings are important for the development of sustainable electronic devices like organic solar cells.

5. References

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